[0001] DEVICE AND METHOD FOR NON-DISPERSIVE CONTACTING OF LIQUID-LIQUID REACTIVE SYSTEM

[0002] FIELD OF THE INVENTION

[0003] The present invention relates to an improved method and device for non-dispersive contacting of liquid-liquid reactive system. In particular, the present invention relaxes to a process and an apparatus for separating impurities from a liquid by a non-dispersive contacting of liquid-liquid reactive systems, said liquids being immiscible with each other.

[0004] BACKGROUND OF THE INVENTION

[0005] There ~~are~~ are many impurities/~~contaminant~~ contaminants present in the downstream hydrocarbon products like LPG, gasoline, naphtha, kerosene, diesel etc, from petroleum crude processing units. These contaminants appear in hydrocarbon products due to natural ~~source~~ sources or ~~produce~~ are produced during ~~passing~~ passage through different processing stages. The impurities like napthenic acid ~~in~~ in diesel, hydrogen sulfide, mercaptans and COS in gasoline, LPG, naphtha and kerosene obtained from different units are required to be removed to meet the desired specifications which are becoming more and more stringent ~~In~~ in order to meet the environmental statutory regulation.

[0006] These hydrocarbons are treated with either caustic or amine solution, or by both, in a contactor. As will be apparent to a person skilled in the art, ~~&~~ a contactor should ensure proper contacting of immiscible liquid-liquid ~~system~~ systems. Such contactors could be a packed column, tray column, mixing valve or static mixer depending on specific application. For example, for removing H_2S/mercaptan from a hydrocarbon stream, a mixing valve is used. In a mixing valve, one phase gets dispersed into the other phase as droplets, at the expense of shear energy. In this process, the ratio of hydrocarbon and caustic phase is important for maintaining efficiency of the

process. Such process is effective when the reaction of the impurities with the second liquid is very fast, However, such processes suffer carryover of the dispersed phase along with the continuous phase. All these processes ~~generates~~ generate a certain degree of turbulence between the phases.

[0007] Contactors are also known in which minimum turbulence is generated in the contact zone, ~~Such~~ such contactors are made of fibre bundles (US Patent Nos: 3,754, 377; 3,758,404; 3,839,487 and 5,904,849). In such contactors, a series of thin fibre strands are housed in a column. ~~(~~US Patent: 3,758,404~~)~~ describes one such arrangement and US Patent 3,992,156 describes an improved contactor. ~~Further improvement is claimed to have been achieved in US Pat. 3,992,156.~~

[0008] For certain ~~application~~ applications, for e.g. removal of napthenic acid from diesel, the above contactors other than fibre film ~~contactor~~ contactors can not be used, as turbulence of phases creates an emulsion which is stabilized by the sodium naphthenate, which acts like a surfactant. Sodium naphthenate is formed during reaction of caustic with ~~napthenic~~ naphthenic acid. Conventional contactors, e.g. mixing ~~valve~~ valves, static ~~mixer~~ mixers [[*]] do not work due to emulsion formation. Even with fibre film ~~contactor~~ contactors, using a conventional distribution system, emulsification could not be avoided. Therefore, there ~~U~~ is an urgent need for developing a novel distribution system to ensure that turbulence in the interface of caustic and hydrocarbons is avoided.

[0009] Napthenic acids are the main contributors to acidity of the diesel. The napthenic acids react with caustic according to the following equation.

[0010] R-COOH + NaOH [[-]] ≡ R-COONa + H_2O

[0011] The sulfur compounds such as hydrogen sulfide and mercaptans react with caustic according to the equations as follows:

[0012] H_2S+~~2~~2NaOH= ~~RSNa~~ Na_2S+ 2H_2O

[0013] RSH + ~~2~~NaOH = ~~Na_2S~~ RSNa+2H_2O

[0014] Depletion rate of impurities is controlled by mass transfer rate as reaction rate is very high.

[0015] The mass transfer rate of reacting species can be expressed as: R[[-]] =(k)(AXAC) Where

[0016] k mass transfer coefficient,

[0017] A Interfacial area,

[0018] AC concentration gradient

[0019] In conventional treating ~~mechanism~~ mechanisms, devices such as mixing valves and static mixers create an interfacial area by dispersive mixing, which generate droplets[[,]]. To maximize the surface area ~~from~~ for a given volume, considerable shear energy must be imparted to form as many small droplets as possible. Also droplet size has to be as small as possible. Small droplets, however, have the disadvantage of taking a longer time to separate from the bulk phase. Consequently, a large separator is provided.

[0020] The Continuous Film Contactor (CFC) is a static contacting device that produces non-~~dipersive~~ dispersive contacting of the caustic and hydrocarbon phases and improves the removal of acidic/sulphidic impurities from hydrocarbon streams. This prevents emulsion formation and results in minimum caustic carry over and high utilization of caustic solution,

[0021] The contactor, containing fibers, provides a large interfacial area, which increases the mass transfer rate. At the same time, the aqueous phase is constrained to the fibre material by [["]] surface tension, forming a film ~~oo~~ on each fibre that contacts, but never mixes with, the hydrocarbon phase. Consequently, separation of phases becomes a simple and efficient step in the process.

[0022] The efficiency of the mass transfer of undesirable contaminants from hydrocarbon phase to aqueous phase depends on the distribution of both of the liquid phases into the fibre packing. Also, packing of fibers and the fibre holding arrangement play an important role. Packing of fibers should be in such a way that it is equally and evenly distributed across the cross section

and throughout the column length, so that caustic and hydrocarbon in any portion of the column should not pass without seeing each other. The ~~interracial~~ interfacial area of mass transfer depends upon how the column is packed i.e., fibre diameter, number of fibers.

[0023] OBJECTS OF THE INVENTION

[0024] It is an object of the invention to a provide a distribution system for processing hydrocarbon containing ~~naphthemic~~ naphthenic acid with caustic without forming an emulsion.

[0025] It is another object of the present invention to enhance the performance of the distribution system by optimizing operating parameters e.g. temperature, caustic concentration, etc.

[0026] It is yet another object of the present invention to improve performance of a contactor by ensuring complete wetting of fibers before the hydrocarbon phase is introduced

[0027] It is still another object of the present invention to provide a process for removal of impurities where it requires less ~~tune~~ time ~~from~~ for phase separation, less space, less energy and less operating cost and better product specification with respect to removal of contaminants/ impurities.

[0028] It is still another object of the present invention to provide an apparatus for carrying out the process of the present invention.

[0029] It is still another object of the present invention to provide a novel distribution system to ensure that turbulence in the interface of caustic and hydrocarbons is avoided.

[0030] As a whole the overall object of the present invention is to develop a novel process and mass transfer equipment which can be used for removal of undesirable contaminants/impurities like, naphthenic acid, hydrogen sulphide and mercaptans, etc. present in product hydrocarbon streams like ~~LPO~~ LPG, gasoline, naphtha, diesel, kerosene, etc.

[0031] SUMMARY OF INVENTION

[0032] The present invention relates to a novel distribution system for hydrocarbon and caustic for a contact in a contactor containing fibers. The distribution system consists of two stages ~~of~~ in the distributor. This system allows complete wetting of the fibre ~~with~~ during the aqueous phase and before the hydrocarbon phase is introduced.

[0033] BRIEF DESCRIPTION OF THE FIGURES

[0034] Fig. 1 represents the general assembly of a Fibre Film Contactor (FFC) with all accessories such as a distributor, fibre support, etc, fitted on a separator vessel with inlet and outlet provisions.

[0035] Fig. 2 depicts the general assembly of liquid distributors for aqueous and organic phase (2-stage distributor), fibre support.

[0036] Fig. 3A describes the details of the first stage distributor and tube sheets.

[0037] Fig. 3B describes the details of the second stage distributor and tube sheets.

[0038] Fig. 4 depicts the details of a fibre support/ holder, rings, rods for fibre tie up.

[0039] Fig.[[,]] 5 represents the overall assembly of the column, sleeve, distributors and fibre holder.

[0040] Fig. 6 depicts the overall arrangement of contactor and separator used in a commercial plant.

[0041] DETAILED DESCRIPTION OF THE PRESENT INVENTION

[0042] Accordingly, the present invention provides an apparatus for separating impurities from a liquid by ~~a~~ non-dispersive contacting of ~~a~~ liquid-liquid reactive systems, said liquids being immiscible with each other, which comprises a cylindrical column separated into a first stage and a second stage, a plurality of modules of packed metallic fibers mounted in the first stage of said column on a support, a first distributor provided in the first

stage of the column for distributing a first liquid located above said support such that said first liquid completely wets said fibers by capillary action and forms a film thereon, a second distributor fitted at a bottom portion of the second stage for distributing a second liquid containing impurities on to the metallic fibers, wherein said second liquid ~~flow~~ flows ~~co-currently~~ concurrently with said first liquid so that the impurities present in said second liquid react with said first liquid and dissolve therein, and a separator connected to a bottom of said column ~~for separating~~ separates the first liquid and purified second liquid.

[0043] In an embodiment of the present invention, the first distributor separates the cylindrical column into a first stage and a second stage in addition to distributing the first liquid.

[0044] In another embodiment of the present invention, the packed metallic fibers ~~comprises~~ are comprised of fine wires packed in a single or multiple tubes in order to enable mass transfer and/or mass transfer with chemical reaction to take place.

[0045] In yet another embodiment of the present invention, said modules ~~comprise~~ are comprised of a plurality of tubes held inside a metallic shell, said shell being supported either on said separator or independently outside said separator.

[0046] In still another embodiment of the present invention, the modules are supported in said column at their upper ends.

[0047] In one more embodiment of the present invention, the modules are suspended from tie rods mounted in said first stage of said column and the metallic fibers are supported and looped around said tie rods.

[0048] In ~~one~~ another embodiment of the present invention, the metallic wires are packed in the ~~form~~ shape of a sinusoidal wave so that inter fiber void space is uniformly maintained.

[0049] In a further embodiment of the present invention, the metallic fibers are chemically treated to enhance wettability.

[0050] In another embodiment of the present invention, the metallic fibers are made of materials selected from stainless steel, phosphorous bronze, glass fibers and plastic materials.

[0051] In yet another embodiment of the present invention, the metallic fibers ~~are of the~~ have a thickness in the range of from 0.1 mm to 0.3 mm.

[0052] In still another embodiment of the present invention, the modules of metallic fibers ~~comprise~~ are comprised of multiple tubes with a cap on top ~~in~~ of each tube, said cap being provided with an orifice designed for specific flow range.

[0053] In one more embodiment of the present invention, the first distributor is provided with a plurality of holes whose diameter is equal to or greater than the diameter of the packed metallic fibers.

[0054] In ~~one~~ another embodiment of the present invention, the second distributor is provided with a plurality of holes whose diameter is equal to or greater than the diameter of the packed metallic fibers and a plurality of holes of smaller diameter which are placed adjacent to the holes whose diameter is equal to or greater than the diameter of the packed metallic fibers.

[0055] In a further embodiment of the present invention, the separator provided at the bottom of the column is optionally provided with heating coils.

[0056] The present invention also provides a process for separating impurities from a liquid by ~~a~~ non-dispersive contacting of liquid-liquid reactive systems which comprises distributing a first liquid over a support consisting of packed metallic fibers mounted in the first stage of a two stage liquid distributor so that the entire support is completely wetted by said first liquid by capillary action, said first liquid forming a film over said support, distributing separately, a second liquid containing impurities to be removed, said second liquid being immiscible with said first liquid and flowing ~~co-currently~~ concurrently ~~to~~ with said first liquid so that the dissolved

impurities in said second liquid react with the film forming first liquid and dissolve therein, ~~allowing~~ the two liquids to ~~flow~~ flowing downward to a separator and collecting the pure second liquid and, if ~~desires~~ desired, recycling said first liquid.

[0057] In an embodiment of the ~~resent~~ present invention, the first liquid is selected from a caustic solution or amine solution or both and said second solution is a hydrocarbon stream.

[0058] In another embodiment of the present invention, the hydrocarbon stream is selected from LPG, gasoline, naphtha, kerosene and diesel.

[0059] In yet another embodiment of the present invention, the impurities present in the second liquid are naphthenic acid, hydrogen sulfide, mercaptans and COS.

[0060] The present invention also relates to holding of fibers in the distributor in a novel way as modules and each module ~~Is~~ is separately irrigated with caustic. ~~Holding of~~ The apparatus for holding fibers is an integral part of the distributor.

[0061] The present invention also relates to optimization of process parameters for enhancing performance of distribution system and removal of ~~naphthemic~~ naphthenic acid from hydrocarbon phase without formation of emulsion.

[0062] As a whole, the present invention relates to the development of special nondispersive type mass transfer equipment and its internal components, ~~Efficiency~~ wherein efficiency of the process depends on the efficiency of the ~~equipments~~ equipment.

[0063] A new and improved equipment is provided for effective contact between two immiscible liquids to obtain efficient mass transfer with reaction. The increased surface area in CFC compared to conventional contacting ~~device~~ devices, including mixing ~~valve~~ valves, improves the mass transfer rates between the two phases.

[0064] Thus, the present invention discloses an apparatus called Continuous Film Contactor (CFC) and a method for efficient contacting of immiscible liquid - liquid reactive system. ~~It is an~~ The apparatus, consisting of a novel two stage liquid distributor ~~which~~, ensures a smooth continuous film of liquid over a support consisting of stainless steel (SS) fibres arranged in a way such that capillary action of wetting liquid is ensured. ~~Second~~ A second liquid, distributed separately, flows ~~co-currently~~ concurrently and the dissolved component from this stream ~~react~~ reacts with the film forming liquid and dissolves.

[0065] Alternatively, dissolved ~~Impurities~~ impurities from the aqueous phase may be extracted by the hydrocarbon phase. The distribution system allows minimum drag of the flowing liquid over film liquid and no turbulence is generated, which may cause emulsification in certain processes. Disclosed is a process for enhancing performance of a distribution and contactor system.

[0066] A Continuous Film Contactor (CFC) is a static contacting device in which mass transfer occurs in a ~~co-current~~ concurrent flow of a liquid-liquid system through a column tightly packed with fine proprietary metallic ~~fibre~~ fibres. It has wide applications in the petroleum refinery field for treatment and purification of the products obtained from the main stream and also in other fluid handling [["]] industries, It provides the flexibility to meet both today's and tomorrow's environmental regulations ~~on~~ regarding sulphur and other contaminants.

[0067] The present invention relates to a proprietary design of aqueous and hydrocarbon phase distributors (2-Stage), a fibre holding arrangement, and ~~as~~ a whole design of a complete system for removal of hydrogen sulphide, mercaptan and other contaminants, such as sulphur compounds from LPG and similar hydrocarbon ~~stream~~ streams and neutralization of naphthenic acid in diesel and thiophenol from light cycle oil using aqueous caustic solution. The application is not limited to caustic-hydrocarbon contacting.

The invention could be used for any liquid-liquid system such as a hydrocarbon-amine solution of water.

[0068] Accordingly, the present invention provides a process for separating impurities from a liquid by a non-dispersive contacting of liquid-liquid reactive systems which comprises distributing a first liquid over a support consisting of packed metallic fibres mounted in the first stage of a two stage liquid distributor so that the entire support is completely wetted by said first liquid by capillary action, said first liquid forming a film over said support, distributing separately, a second liquid containing the impurities to be removed, said second liquid being immiscible with said first liquid and flowing ~~co-currently to~~ concurrently with said first liquid so that the dissolved impurities in said second liquid ~~reacting~~ react with the film forming first liquid and ~~dissolving~~ dissolve therein, ~~allowing~~ the two liquids ~~to flow~~ flowing downward to a separator and collecting the pure second liquid and, if desired, recycling said first liquid.

[0069] The present invention also provides apparatus for separating impurities from a liquid by a non-dispersive contacting of liquid-liquid reactive systems, said liquids being immiscible with each other, which comprises a cylindrical column, a plurality of modules consisting of packed metallic fibres mounted in the first stage of said column on a support, a ~~flrsi~~ first distributor for distributing a first liquid located above said support so that said first fluid completely wets said fibres by capillary action and forms a film thereon, a second distributor for distributing said second liquid containing said impurities fitted at the bottom of said support, said second liquid flowing concurrently ~~co-curreatly~~ [[-]] with said first liquid so that the impurities present in said second liquid react with said first liquid and dissolve therein, and a separator, connected to the bottom of said column for separating the first liquid and said purified second liquid. ~~Brief description of the drawings~~

[0070]

[0071] ~~BRIEF DESCRIPTION OF THE FIGURES~~

[0072] ~~Fig. 1 represents the general assembly of a Fibre Film Contactor with all accessories like distributor, fibre support etc, fitted on a separator vessel with inlet and outlet provision.~~

[0073] ~~Fig. 2 depicts the general assembly of liquid distributors for aqueous and organic phase (2 stage distributor), fibre support.~~

[0074] ~~Fig. 3A describes the details of the 1st stage distributor and tube sheets.~~

[0075] ~~Fig. 3B describes the details of the 2nd stage distributor and tube sheets.~~

[0076] ~~Fig 4 depicts the details of fibre support/ holder, rings, rods for fibre tie up.~~

[0077] ~~Fig, 5 represents the overall assembly of the column, sleeve, distributors and fibre holder.~~

[0078] ~~Fig. 6 depicts the overall arrangement of contactor and separator used in a commercial plant.~~

[0079] The related art of ~~In fig~~. Fig. 1 comprises contactor C1, wherein ~~C-01~~ (6) ~~is~~ a vertical glass contactor consisting of treated stainless steel (SS) fibers (7). Caustic and diesel are introduced into the contactor (6). Caustic is introduced through a distributor (5). Diesel from tank V2 is a continuous phase and is introduced ~~from~~ into the side of contactor (6). Caustic flows preferentially around SS fibers (7). The contactor (6) is located on top of a glass separator S1 in which the caustic and hydrocarbon phase separate.

[0080] In the present distribution system it was observed[[,]] that emulsion is formed at the point where caustic and diesel meet. The emulsion formation continues up to the separator (8) and does not separate at all. This creates carry over of diesel in caustic and caustic in diesel. The reason for emulsion formation is basically generation of turbulence at the interface. Hydrocarbon phase comes out from the top of the separator (8) through hydrocarbon line (9) and contaminated caustic is taken out from the bottom

of the separator (8) through line (10). ~~Provision of~~ An electrical heating arrangement (11) is provided in the separator (8).

[0081] Subsequently, a novel distributor system consisting of two stages as shown in ~~fig.~~ Fig. 2 was developed. The distributor comprises ~~of~~ fibers held together as modules (13). Each module (13) is separately irrigated with caustic. Aqueous caustic solution enters through nozzle (15) and is distributed in the caustic distributor (14). Fibers (7) are supported from tie rods (22) and the tie rods are fixed on the ring (21), as shown in Fig. 4. Sufficient height is provided in each module to allow complete wetting of the fibers with caustic. Details of the caustic distributor ~~is~~ are shown in the top view of ~~fig.~~ Fig. 3A. This is followed by distribution of diesel in the second distributor (19) located below caustic distributor (12). Diesel is fed so as to be distributed uniformly such that no turbulence occurs. Since the fibers are already wetted with caustic, drag force created by diesel flow can not dislodge caustic from, the fibers. At least two ~~vents~~ vent nozzles (16,18) are provided at two zones of the distributor. ~~Bach~~ Each module (13) of fibers passes through tube sheet-A (20).

[0082] In the novel distribution system of the present invention, no emulsion formation was observed in any part of the contactor and separator, ~~Process~~ The process was further optimized by manipulating the temperature of caustic ~~&~~ and diesel, and the flow ratio of diesel and caustic.

[0083] The system of the present invention was used to evaluate the performance of the equipment. Different ~~type~~ types of diesel of TAN value ~~varies~~ varying from 0,5 to 0.7 mg KOH/gm of diesel (~~Acidity~~ acidity due to ~~naththenic~~ naphthenic acid content) have been tested for ~~napthenic~~ naphthenic acid removal, product ~~is~~ being obtained with TAN value of 0.025 to 0.087 mg KOH/gm of diesel[[,]]. It was well below the maximum limit of ~~15~~ 0.15 mg KOH /gm diesel of TAN value.

[0084] ~~A New~~ New and improved equipment/internals are tested for effective contact between two immiscible liquids to obtain efficient mass

transfer with reaction. The increased surface area in the CFC compared to conventional contacting ~~device~~ devices, including mixing ~~valve~~ valves, improves the mass transfer rates between the two phases. The continuous film contactor is a cylindrical column (23,25) in which metallic fibers (7) are ~~hanged by~~ hung on a support (12), ~~up to~~ and extend to the inside of the separator (8) at the bottom of the contactor (23,25) (~~Fig.~~ Figs. 5,6). The aqueous phase distributor (14) is fitted at the top of the fibre holder/support (12) and the hydrocarbon phase distributor (19) is fitted at the bottom of the fibre support (Fig. 2). Initially, metallic fibers are wetted by passing aqueous caustic solution through distributor (14) from the top of the fibers, then the hydrocarbon phase is fed separately through the other distributor[[)]]. The two phases flow down ~~co-currently~~ concurrently through the contactor (25,7) ~~at~~ as thin ~~film~~ films, the reaction ~~occurs~~ occurring at the surface. The mass transfer of the reactants from the bulk phase to the interface and the transfer of the products from the interface to the bulk phase are enhanced due to thinness of the films[[,]]. ~~As both the~~ Both phases flow down to the separator (8), and they are separated there. The bottom aqueous phase is re-circulated by pump (24) and fed to ~~1st~~ the first stage caustic distributor (14) through nozzle (15).

[0085] The present invention will now be described with reference to the following non-limiting ~~Example~~ example.

[0086] Example 1:

[0087] The ~~naphtheaic~~ naphthenic acid content of ~~NO~~ NG diesel (140-390 °C) is much higher (0.6 mg KOH/gm or 0.256 wt %) than the recommended limit (0.15 ~~nag~~ mg KOH/gm or 0.05 ~~wtVo~~ wt%)[[,]]. The described embodiment is used in the general assembly (~~Pig.~~ Fig. 1) for this experimentation. Caustic solution is fed from the top of the contactor through the distributor (~~Fig.~~ Figs. 2, 3A) (14) and NG diesel is fed through hydrocarbon ~~feed~~ nozzle ~~(1?)~~ (17) and distributed through hydrocarbon distributor (~~Fig.~~ Figs. 2,3B) (19). A thin ~~Thin~~ layer ~~is~~ is formed on the fibre

(7) surface with aqueous caustic solution and diesel ~~passes~~ concurrently passing downwards along the film ~~co-currently~~. Purified diesel is withdrawn from the top phase ~~k~~ of the separator (8). The TAN value of diesel was obtained as 0.022 to 0.087 mg KOH/gm or 0.286 wt% TAN value.

[0088] ~~The different~~ Different operating parameters were used for the process. These are as follows:

[0089]	Optimum caustic concentration	0.5-3%
[0090]	Caustic: Diesel flow ratio	1:10-1:20
[0091]	Operating temperature	40 to 46° C
[0092]	Distributor	2 Stage
[0093]	Residence time in separator	10-30 mins.
[0094]	Type of fibre	Stainless Steel
[0095]	Treatment	Chemical
[0096]	Shape	Sinusoidal

[0097] The experiment was repeated with a bigger size contactor in which re-circulation of caustic was maintained.

[0098] The caustic solution is pumped and filled in the separator (8). The caustic solution is then recycled from separator (8) and distributed over the top of the continuous ~~Film Contactor~~ film contactor (CFC) through the caustic distributor 14 (~~Fig.2&3A~~ Figs. 2 and 3A). The hydrocarbon is pumped and distributed through hydrocarbon distributor 19 (Fig.3B), where fibre ~~bundle~~ [[*]] bundles (13) are supported from the top and ~~hanged~~ hung inside the sleeve (25) ~~up to bottom of~~ and extend into the separator (8). The caustic solution wets the fibres (7) preferentially and flows downwards to the bottom of the separator (8)[[,]]. The hydrocarbon also flows downward forming a layer around the caustic wetted fibres. The naphthenic acid present in the hydrocarbon ~~dissolve~~ dissolves in the caustic phase around the fibres (7) in the contactor (25).

[0099] The treated hydrocarbon and caustic solution are separated in the separator (8). The caustic solution from separator (8) is recycled back to

the contactor ~~till~~ until the depletion of concentration of caustic solution below 2 wt%. Purified hydrocarbon is withdrawn from the top phase in the separator (8).